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OXIDATION AND REDUCTION OF IODINE UNDER THE ACTION OF ULTRASONIC WAVES

I. Ye. El piner, M. F. Kolesnikova Lab of Biochem of Cancer Acad Med Sci USSR Presented by Acad A. N. Frumkin 25 Oct 1950

The research on the application of ultrasonic waves carried out by this group of investigators at the Laboratory of the Biochemistry of Cancer, Academy of Medical Sciences USSR, may be of interest from two different points of view. As stated by the authors, ultrasonic waves bring about oxidation of amino acids. Because this oxidation is selective, a therapeutic effect in the treatment of cancer may conceivably be expected. The liberation of iodine, introduced in the form of potassium iodide, would enhance any therapeutic effect which is due to oxidation. On the other hand, an accumulation of free and organically bound iodine in the tissue of malignant tumors probably would make the tumor relatively opaque to X-rays and thus facilitate diagnosis. While the authors do not mention the purpose of the investigation launched by them, either or both of these possibilities must be strongly considered.

The reference to similarities and differences between the ionizing effect of ultrasonic waves and that of particle and high-frequency electromagnetic radiation is of interest.

Oxidation and reduction resulting from the action of ultrasonic waves have been observed by many investigators (1-3). It has been established that under the action of such waves, sulfur is liberated by hydrogen sulfide, free iodine by potassium iodide, ferrous sulfate is oxidized to ferric sulfate, etc. The phenomenon of oxidation due to the action of ultrasonic waves not only occurs with solutions of inorganic acids and salts, but also has been observed with organic compounds. As shown in previous investigations (4), a number of amino

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acids have been decomposed in the same way. Principally, amino acids of aromatic and cyclic structure were broken down. Moreover, we succeeded in identifying aspartic acid as one of the products of the splitting up of histidine. The latter has provided a basis for us to advance the hypothesis that the decomposition of amino acids evidently depends on the exidation processes which take place in an aqueous solution treated by sound waves.

The oxidizing action of ultrasonic waves is ordinarily attributed to the hydrogen peroxide which appears in the solution. However, the yield of H₂O₂ is too small to explain the oxidation processes. All chemical reactions involving ultrasonic waves are evidently secondary in the sense that they are closely linked with the appearance of activated water molecules and strongly oxidizing products of the decomposition of these molecules. The experimental evidence which we have obtained testifies to this. Figure 1 gives the curve showing the dependence of the quantity of iodine, formed through oxidation by ultrasonic waves, on the concentration of potassium iodide in the solution. The solution was treated for 30 minutes with ultrasonic waves of a 600,000-cps frequency which were produced by a piezoelectric-quartz-crystal oscillator with a power input of the order of 5 w/sq cm. The quantity of iodine was determined by titration of the solution with hyposulfite, both before and after application of the ultrasonic waver.

The curve in Figure 1 shows that under identical physical conditions of ultrasonic wave application, the quantity of liberated iodine increases as the concentration increases only when the concentration of potassium iodide in the solution is relatively low. In potassium iodide solutions of higher concentration, the quantity of liberated iodine remains constant.

The curve in Figure 2 shows in percent the dependence between the ratio of the quantity of liberated icdime to the content of iodide ions in the solution and the concentration of potassium iodide. It is evident that this ratio increases as the solution is made more dilute.

We detected still another phenomenon, a screening effect. Thus, the oxidation of iodime, brought about by ultrasonic waves, is significantly depressed when tryptophan is present. Tryptophan is very easily decomposed under the action of ultrasonic vibrations (4), and this protects the iodine ions from oxidation. The screening phenomenon is already very evident at a tryptophan content of 0.2% in a 2 N solution of I, even when the vibrations are applied for as long as 60-90 minutes.

It should be noted further that the ultrasonic oxidation of iodine does not occur if the potassium iodide solution has been previously saturated with hydrogen. In cases of this type we failed to detect free iodine, even enter intensive action of ultrasonic waves for several hours.

Furthermore, it appeared that when a solution saturated with gaseous hydrogen was subjected to the ultrasonic treatment, any molecular iodine present in the solution was reduced. By this method we succeeded in reducing almost completely 2.85 t 10⁻⁴ gram of iodine dissolved in 1 ml of a 2 N aqueous solution of KI. It should be emphasized that the ultrasonic reduction of iodine takes place extremely slowly. For the reduction of the above-stated quantity of iodine, the solution had to be treated ultrasonically for 4 hours.

The reduction of iodine evidently takes place in the gaseous phase, i.e., in the gas bubbles which are formed under the influence of the ultrasonic waves. When such a solution is exposed to ultrasonic waves after being saturated with hydrogen, the molecular hydrogen and molecular iodine, together with water vapor, will diffuse into the spaces formed by cavitation. Under these conditions, iodine will be ionized simultaneously with the process of hydrogen ionization.

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Both of the above-described phenomena (splitting and screening), which we detected while studying the liberation of iodine under the action of ultrasonic waves, can evidently be explained by the activation and ionization of water molecules and the appearance of products of splitting. In other words, the chematical processes which we observed were most probably dependent on the formation in the solution of products of the decomposition of water which possess high reactive capacities (HO, H, HO₂, H₂O₂, etc.).

The splitting of water molecules evidently takes place in the gaseous phase, in gas bubbles. The rapid bursting of the bubble contributes to the scattering of the radicals and molecules formed in the liquid phase of the solution, and these molecules and radicals interact with the substances dissolved in the solution. (The formation of splitting products of water under the influence of ionizing radiations of high-energy alpha and beta particles, gamma rays, etc., is known to occur directly in the liquid phase of the irradiated solution).

If free radicals are really formed in gas bubbles produced by cavitation during the application of ultrasonic waves, then free electrical charges must develop in these bubbles. A number of investigators (6-8) have indicated that large electrical voltages are present in cavitations. Furthermore, experimental data has been cited in literature which show that water decomposes under the influence of ultrasonic waves (9). After the prolonged action of this physical agent on water in an inert gas atmosphere, the authors succeeded in detecting oxygen and hydrogen in the molecular state.

This hypothesis, that under the influence of ultrasonic waves water breaks down into products which possess oxidizing or reducin, properties, explains satisfactorily not only the experimental data which is cited in this article and which we obtained, but also a number of other chemical processes which take place as a result of the action of ultrasonic waves.

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Appended figures follow.7

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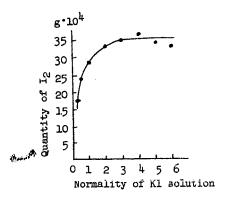
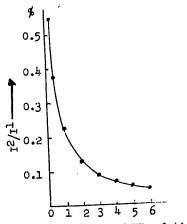


Figure 1. Dependence of quantity of liberated iodine on concentration of potassium iodide in solution.



Normality of KI solution

Figure 2. Dependence between the ratio of the quantity of liberated iodine (I²) to the content of iodine ions in the solution (I¹) and the concentration of potassium iodide.

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